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裂叶翼首花的化学成分

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CHEMICAL CONSTITUENTS FROM PTEROCEPHALUS BRETSCHNEIDRI

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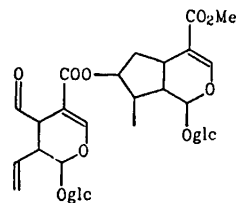
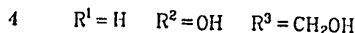
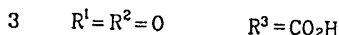
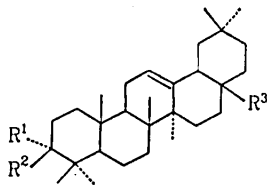
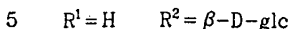
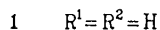
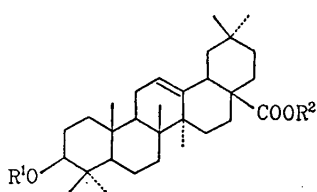
关键词 川续断科; 裂叶翼首花; 三萜; 环烯醚萜甙

Key words Dipsacaceae; *Pterocephalus bretschnidri*; Triterpenoids; Iridoidal glycosides

裂叶翼首花(*Pterocephalus bretschneldri* Pritz)是川续断科(Dipsacaceae)翼首花属植物,广泛分布于中国西南地区,民间用其全草治疗风湿感冒等疾病,在藏族聚集地区,其块根称岩七,有滋补健身功效^[1].

前文^[2]我们曾报道从裂叶翼首花乙醇提取物的正丁醇部分得到两个新的三萜皂甙,裂叶翼首花皂甙 A(bretschnoside A)和裂叶翼首花皂甙 B(bretschnoside B).从其酯溶性提取部分我们分离得到 11 个化合物,分别鉴定为齐墩果酸(oleanolic acid)(1),齐墩果酸甲酯(methyl oleanolate)(2),古柯二醇(erythrodiol)(3),3-oxo-oleanolic acid(4),oleanolic glucoside(5),loganin(6),cantleyoside(7),胡萝卜甙(daucosterol)(8), β -谷甾醇(β -sitosterol)(9)以及咖啡酸(caffeic acid)(10),硬脂酸(stearic acid)(11).

化合物 1—4 是齐墩果烷型三萜,5 与从竹节参(*Panax japonicum*)中分离到的齐墩果酸-28-O- β -D-葡萄糖甙一致^[3].化合物 6 和 7 属于单萜环烯醚萜甙,其中 7 是二聚环烯醚萜甙,曾从同科植物 *Dipsacus sylvestris* 中得到^[4].



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实验部分

熔点用 Kofler 熔点仪测定,温度未校正;IR 用 PE-577 型光度计测定, KBr 压片;UV 用 UV-210A 光度计测定, EtOH 为溶剂;MS 用 Finnigan-4510 质谱仪测定, EI, 70eV; 1H , ^{13}C NMR 在 Bruker AM-400 超导核磁共振仪上测定。

实验样品于 1990 年 8 月采自四川省乡城县,裂叶翼首花根粉 4.2kg,以工业酒精冷浸三次,合并浸取液浓缩,依次用石油醚(60-90 $^{\circ}$)、乙酸乙酯、正丁醇萃取。石油醚及乙酸乙酯萃取部分经硅胶柱层析得到化合物 1(870mg, 0.021%), 2(75mg, 0.0018%), 3(16mg, 0.00038%), 4(35mg, 0.00083%), 5(420mg, 0.010%), 6(12.5g, 0.30%), 7(8.2g, 0.19%), 8(500mg, 0.012%), 9(326mg, 0.0078%), 10(200mg, 0.0048%), 11(156mg, 0.0037%)。

齐墩果酸(1) $C_{30}H_{48}O_3$, 白色针晶, mp 306-307 $^{\circ}C$. 和标准品对照, TLC, IR 完全一致。

齐墩果酸甲酯(2) $C_{31}H_{50}O_3$, 白色针晶, mp 210-213 $^{\circ}C$. MS(m/z): 470(M^+), 439, 260(base), 248, 203. 1H NMR($CDCl_3$)(δ , ppm): 3.52(3H, s, OCH_3), 5.29(1H, t, $J = 3.0$ Hz). ^{13}C NMR($CDCl_3$)(δ , ppm): 38.1, 23.6, 78.7, 38.7, 55.2, 18.3, 32.6, 39.3, 47.6, 37.0, 23.1, 122.1, 143.4, 41.6, 27.7, 23.4, 46.6, 41.3, 45.8, 30.6, 33.8, 32.3, 28.1, 16.8, 15.3, 16.8, 25.8, 177.8, 33.1, 23.6, 51.4.

古柯二醇(3) $C_{30}H_{50}O_2$, 白色针晶, mp 232-234 $^{\circ}C$. MS(m/z): 442(M^+), 426, 412, 203(base), 133. 1H NMR($CDCl_3$)(δ , ppm): 3.25(1H, m, $3\alpha\text{-H}$), 5.13(1H, t, $J = 3.6$ Hz), AB system [3.52(1H, d, $J = 11$ Hz), 3.18(1H, d, $J = 11$ Hz), 28- CH_2OH]. ^{13}C NMR($CDCl_3$)(δ , ppm): 138.7, 125.0, 79.0, 69.9, 55.1, 54.0, 47.6,

46.8, 42.0, 40.0, 39.4, 39.3, 38.7, 38.0, 36.8, 35.2, 33.7, 32.8, 30.6, 28.1, 27.2, 26.0, 23.3, 23.3, 21.3, 18.3, 17.3, 16.7, 15.7, 15.6^[5].

3-Oxo-oleanolic acid(4) $C_{30}H_{46}O_3$, 白色针晶, mp 282–284°C. MS(m/z): 454(M^+), 408, 248(base), 203. 1H NMR($CDCl_3$)(δ , ppm): 5.27(1H, br s). ^{13}C NMR($CDCl_3$)(δ , ppm): 217.6(3-oxo), 184.4, 143.6, 122.2, 55.3, 47.4, 46.9, 45.8, 41.7, 40.9, 39.2, 39.1, 36.8, 34.1, 33.8, 33.0, 32.4, 32.1, 30.7, 27.6, 26.4, 25.8, 23.5, 23.4, 22.8, 21.4, 19.5, 17.0, 15.0, 14.1^[6]

Oleanolic glucoside(5) $C_{36}H_{58}O_8$, 白色针晶, mp 235–237°C. 1H NMR(C_5D_5N)(δ , ppm): 6.34(1H, d, $J=8.0$ Hz, glc H-1), 5.45(1H, br s). ^{13}C NMR(C_5D_5N)(δ , ppm): 176.5, 144.2, 123.0, 95.6, 79.4, 79.0, 78.2, 74.2, 71.2, 62.3. The ^{13}C NMR data of its aglycone was very similar with those of oleanolic acid.

Loganin(6) $C_{17}H_{26}O_{10}$ 白色针晶, mp 221–223°C. 它的 IR, MS and NMR 数据与标准品一致.

Cantleyoside(7) $C_{32}H_{44}O_{19}$, 白色粉末, FAB-MS(neg.)(m/z): 732(M^-), 569(M^- -glc), 513, 459, 373, 119. 1H NMR(C_5D_5N)(δ , ppm): 9.80(1H, s, -CHO), 7.72(1H, d, $J=1.0$ Hz), 7.64(1H, d, $J=1.0$ Hz), 5.83(1H, d, $J=4.7$ Hz), 5.66(1H, d, $J=4.0$ Hz), 5.39(1H, d, $J=8.0$ Hz, glc H-1), 5.35(1H, d, $J=7.8$ Hz, glc' H-1). ^{13}C NMR(C_5D_5N)(δ , ppm): 201.0, 167.5, 166.5, 153.1, 151.5, 134.2, 120.1, 112.5, 109.3, 100.9, 97.0, 96.5, 79.1, 79.0, 78.6, 78.6, 77.1, 74.9, 74.8, 71.6, 71.5, 62.8, 62.7, 51.1, 46.6, 44.8, 44.7, 39.9, 39.6, 31.5, 27.3, 13.3.

胡萝卜甙(8) $C_{35}H_{60}O_6$, 白色粉末, mp > 300°C, $IR \nu_{max}^{KBr} cm^{-1}$: 3400, 2940, 1460, 1380, 1070, 960, MS(m/z): 576(M^+), 414(M^+ -glc+H), 396. 其 ^{13}C NMR 光谱比 β -sitosterol 多 β -D-glucose 信号。

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